Spreading of Latex Particles on a Substrate

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Abstract. – We have investigated both experimentally and theoretically the spreading behavior of latex particles deposited on solid substrates. These particles, which are composed of cross-linked polymer chains, have an intrinsic elastic modulus. We show that the elasticity must be considered to account for the observed contact angle between the particle and the solid substrate, as measured through atomic force microscopy techniques. In particular, the work of adhesion computed within our model can be significantly larger than that from the classical Dupré formula.

Introduction. – Adhesion phenomena are of great importance in science and technology[1, 2]. The classical approach to describe the adhesion between two elastic bodies under a compressive force is given by the Johnson, Kendall, and Roberts (JKR) theory[3]. It is essentially an extension of the Hertz theory of elastic contact, allowing for a tensile stress to develop inside contact area to account for the effect of adhesion. For an adhesive sphere of radius R in contact with a flat solid substrate, the JKR theory predicts that the deformation of the sphere at the center of the contact area is $\delta = \frac{a^2}{R}\left[1 - \frac{2}{3}\left(\frac{a_0}{a}\right)^{3/2}\right]$, where a is the contact radius given by $a^3 = \frac{3R}{4K}\left[F + 3\pi RW + \sqrt{6\pi RWF + (3\pi RW)^2}\right]$. Here $a_0 = (9\pi R^2 W/2K)^{1/3}$ is the contact radius at zero force ($F = 0$), W is the thermodynamic work of adhesion[4], K is the rigidity of the sphere $K \equiv E_B/(1-\nu^2)$, E_B is the Young's modulus, and ν is the Poisson's ratio. If $W = 0$, the JKR theory reduces to the Hertz result for elastic contact of a nonadhesive spherical particle with a planar substrate, for which $\delta = a^2/R$[5].

Recent attention has focussed on the adhesion properties of rigid spheres placed on a soft matrices where large deformation occurs. Rimai *et al.* [6] have studied this problem experimentally while Maugis [7] has extended the JKR analysis to large contact radii. In this paper, we consider the "inverse" problem of soft spherical particles adsorbed on a rigid planar substrate, on which they tend to spread and deform under the effect of spreading forces. Our first aim is to present a series of experiments conducted by atomic force microscopy techniques to characterize the shape of isolated latex particles deposited on a clean silicon wafer surface. Using AFM, we determine the equilibrium height of the deformed latex particles, and to deduce

Latex	T_g	GF (%)	N (μmole/g)	R (nm $\pm$ 5 nm)	E_B (Mpa)	γ_s (mJ/m^2)
SB-(-2)-75	-2	75	210	175	0.63	53
SB-(11)-75	11	75	235	167	1.35	46
SB-(28)-75	28	75	225	167	1.92	48
SB-(-2)-92	-2	92	310	148	0.6	54
SB-(-8)-43	-8	43	334	164	2.02	48
SB-(-7)-68 C-	-7	68	190	138	–	45
SB-2-68 C+	2	68	427	148	–	56

TABLE I – *Characteristics of the latex particles: the glass transition temperature T_g, gel fraction (GF), number of acidic function per unit area N, the diameter R, and bulk elastic modulus E_B and surface tension γ_s.*

a contact angle. These experiments demonstrate that the final equilibrium shape of the particle does not depend only on the surface tensions, like for a liquid drop, but is greatly affected by the elastic modulus of the particle. Since in these experiments the particles deformation is rather important, one cannot use the JKR theory which assumes that $a \ll R$. Therefore, in a second step, we present a simple model which predicts the contact angle of an elastic sphere deformed under the effect of spreading forces even for rather large deformation (but still assuming linear elasticity). Very recently, Joanny *et al.* [8] have considered a similar problem of spreading of a "cylindrical" droplet of gel in a regime where the role of surface tension is not important. Here, we consider spherical geometry and explicitly take the surface tension into account, which are more appropriate for our experiments. We point out that a more accurate estimate of W should take into account the elastic energy, which is not contained in the Dupré formula, $W = \gamma_s(1 + \cos\theta)$, which relates the surface tension of a liquid drop γ_s and the contact angle θ to W.

Experimental Investigation of the Spreading Behavior of Elastic Spheres. – The latex particles used in the present study are formed by a soft core of partially crosslinked styrene-butadiene copolymer molecules, surrounded by a thin stiffer shell made of carboxylic co-monomers. The ratio of styrene over butadiene co-monomers in the core allows one to adjust the glass transition temperature T_g of the latex, while the elastic modulus can be varied by adjusting the degree of crosslinking of the core attained during the formation of the particles. In fact, it is not easy to quantitatively determine the elastic modulus of an isolated latex particle. Two quantities can be used to qualitatively estimate this elastic modulus. First, the gel fraction, GF, represents the ratio of insoluble species remaining after swelling the particles in a good solvent of the styrene butadiene copolymers. The larger GF, the higher is the degree of crosslinking and the higher the elastic modulus. However, the correspondence between them is not quantitative, because the crosslinking reaction is accompanied by chain

Latex	R (nm $\pm$ 5 nm)	h (nm)	$2a$ (nm)	θ (°)	W_D (mJ/m^2)
SB-(-2)-75	175	26	640	11	106
SB-(11)-75	167	39	610	22	88
SB-(28)-75	167	49.5	565	32	89
SB-(-2)-92	148	46	398	34	99
SB-(-8)-43	164	15.8	695	6	95
SB-(-7)-68 C-	138	37	365	27	85
SB-2-68 C+	148	23	460	12	111

TABLE II – *Geometrical characteristics of the latex particles adsorbed on silica, as determined through AFM, including the height of the adsorbed particles h, the contact radius a, the contact angle θ and Dupré energy W_D.*

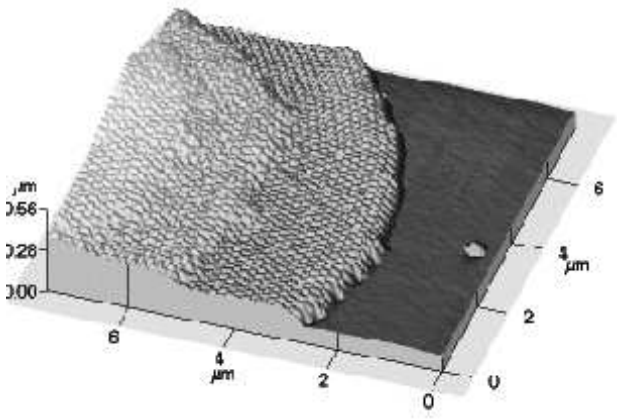

Fig. 1 – AFM image of the edge of a drop of latex (SB-(-2)-75) deposited on a silica surface and dried: an isolated particle is visible on the right of the image.

scissions. Second, the bulk elastic modulus E_B of macroscopic films which can be formed from slowly evaporating the water of a latex suspension can easily be measured. These films are made of closed packed particles, adhering together by their shells. It is, however, not totally obvious that the bulk elastic modulus thus measured corresponds exactly to the elastic modulus of an isolated particle. The characteristics (T_g, GF, E_B, radius) of the latex used are reported in Table I.

In order to investigate the spreading behavior of these latex on controlled surfaces, the latex needs first to be thoroughly washed in order to extract the surfactant molecules used to stabilize the suspension during the synthesis. Then a drop of a highly diluted suspension is deposited on a clean silicon wafer surface [9]. Under slow evaporation of the water, a drop of well organized latex particles forms, with particles arranged successively from the edge of the drop in a closed packed monolayer, and then bi-layer, and then multilayers, as shown in the AFM image (contact mode) of Fig. 1. Ahead of this continuous drop, a few isolated particles remain (Fig. 1), and can be used to characterize the spreading behavior of isolated particles. It is important to note that while we cannot verify that the sol fraction of the particles has been significantly extracted during the washing procedure, using AFM we do not observe any leakage or spreading of this sol fraction ahead of the particle, except perhaps in the case of the latex with the highest sol fraction where some leakage become visible. We thus think that the sol fraction only affects the viscoelastic properties of the particles, and not significantly their spreading behavior. In Fig. 2, AFM images of latex particles with similar glass transition temperatures, similar radius and different GF are reported. It appears clear that the softer particles are more deformed and spread than the harder ones, while all having the same shell should have the same spreading parameter. In Fig. 3, AFM images of latex particles having the same GF and different shells are presented, showing that, with the same elastic modulus, the more polar shell leads to a higher deformation of the particles. These experiments clearly demonstrate that both the surface energy and the elastic modulus of the particles govern their spreading behavior. It is quite easy, from AFM, to quantitatively measure the height h of the deformed particles. Their diameter at the surface can also be measured, but this measurement is far less accurate than that of the height, as it needs to de-convolute from the tip radius R_{tip} [10].

From the geometrical characteristics of the deformed particles a contact angle can be

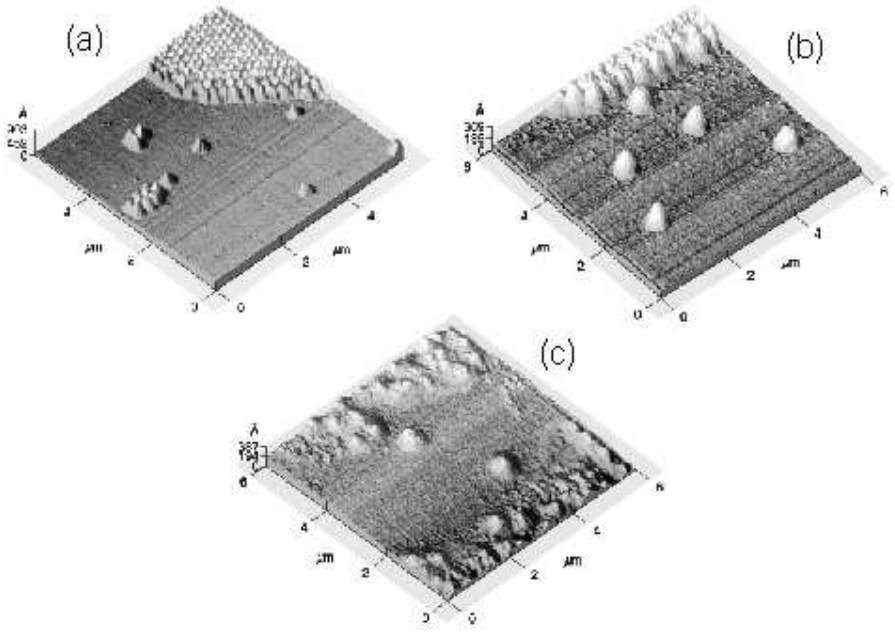

Fig. 2 – Latex particles adsorbed on a silica surface (AFM image, contact mode under a constant load of 5 nN.) (a) Latex SB-(-2)-92, (b) Latex SB-(-2)-75, (c) Latex SB-(-8)-43.

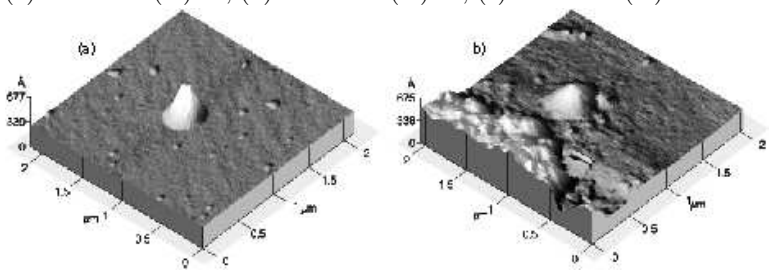

Fig. 3 – Latex particles adsorbed on a silica surface (AFM image, contact mode under a constant load of 5 nN.) (a) Latex SB-(-7)-68 C-, (b) Latex SB-(2)-68 C+.

deduced: assuming that the particles take the shape of a spherical cap, with a radius R_{cap} given by $R_{cap} = (4R_0^3 + h^3)/(3h^2) - R_{tip}$, ($R_0$ is the initial radius of the particle), the contact angle is given by $\theta = \sin^{-1}\left[\frac{1}{2R_{cap}}\sqrt{\frac{2}{3}\left(\frac{16R_0^3}{h} - 2h^2\right)}\right]$. An estimate of the thermodynamic work of adhesion can then be deduced from the Dupré formula. The corresponding data are reported in Table II. While the order of magnitude of W appears reasonable, and comparable to similar data extracted by Unertl *et al.* on different latex [11, 12], it seems clear, however, that owing to the obvious influence of the elastic modulus on the degree of spreading of the different latex we have investigated, it is not correct to analyze this spreading without taking into account the balance between adhesive and elastic energy. This is the aim of the model that we develop now.

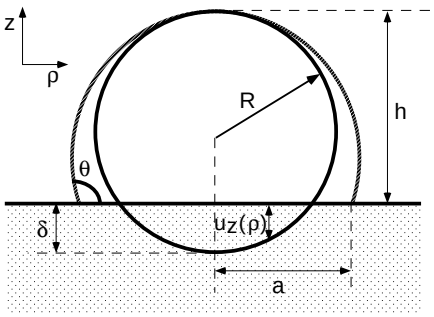

Fig. 4

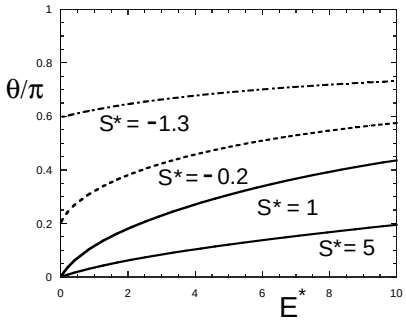

Fig. 5

Fig. 4 – The geometry of a deformed elastic sphere.

Fig. 5 – The contact angle as a function of the normalized elastic modulus $E^* \equiv 2\sqrt{3}KR/(\pi\gamma_s)$ for different values of the reduced spreading parameter $S^* = S/\gamma_s$.

The Model. – Consider an elastic sphere with radius R spread on a high-energy surface. For simplicity, we assume that the sphere deforms into a spherical cap of radius $R_1 = (4R^3 + h^3)/(3h^2) \geq R$, under the constraint that the volume is conserved, where h is the height of the deformed particle. The total energy of the system is the sum of two terms, namely, the surface energy U_s and the elastic energy U_{el}. The surface energy may be written as [1, 4]

$$U_s = -\frac{4\pi}{3} R^2 S \left(\frac{2R}{h}\right) + \frac{4\pi}{3} R^2 (3\gamma_s + S) \left(\frac{h}{2R}\right)^2, \tag{1}$$

where $S \equiv \gamma_{SO} - (\gamma_{SL} + \gamma_s)$ is the spreading parameter. It is easy to check that minimization of U_s with respect to h leads to Young's law $\gamma_{SO} = \gamma_{SL} + \gamma_s \cos\theta$. It describes the contact angle θ of a liquid drop on a solid surface.

For the case of the latex particles, we must take the elastic energy stored into the deformation into account. Unfortunately, even with the simplifying assumption of a spherical cap deformation, a rigorous computation for the displacement field for such a deformation remains a difficult task. Therefore, we must resort to a scaling picture to obtain the elastic energy stored in such a deformation. Consider a deformed elastic sphere shown in Fig. 4; the z-component of the displacement field within the contact area of radius a directly follows from the geometry

$$u_z(\rho) = \delta - R\left[1 - \sqrt{1 - (\rho/R)^2}\right] \approx \delta\left(1 - \frac{\rho^2}{2\delta R}\right), \tag{2}$$

where $\delta \equiv 2R - h$ is the central displacement. Note that due to volume conservation, the contact radius a is determined in terms of the height of the spherical cap h by: $a^2 = \frac{4}{3}R^2\left[\frac{2R}{h} - \frac{h^2}{(2R)^2}\right]$. On the other hand, if an external stress of the form

$$\sigma(\rho) = \sigma_0 \left(1 - \rho^2/a^2\right)^{-1/2} + \sigma_1 \left(1 - \rho^2/a^2\right)^{1/2} \qquad \rho < a, \tag{3}$$

is exerted on the surface of a semi-infinite half-space elastic medium, it will be displaced by an amount[13]

$$u_z(\rho) = \frac{\pi a}{K}\left[\sigma_0 + \frac{1}{2}\sigma_1\left(1 - \frac{\rho^2}{2\,a^2}\right)\right], \tag{4}$$

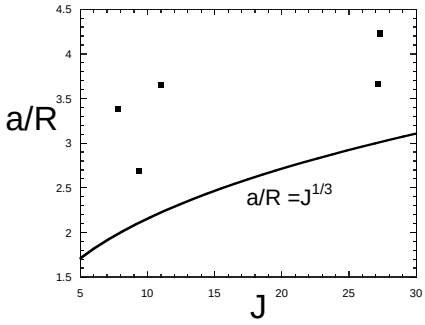

Fig. 6

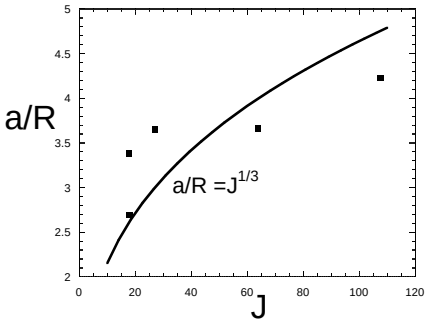

Fig. 7

Fig. 6 – The predicted radius of the contact area using W_D from the Dupré formula. Here, $J \equiv 9\pi W/(2KR)$. Clearly, the predicted contact radii are about 2 times smaller.

Fig. 7 – The predicted radius of the contact area using W from our theory. In contrast to Fig. 6, our prediction is quite good.

where $K \equiv E_B/(1-\nu^2)$ is the rigidity. Comparing Eq. (4) to Eq. (2), we obtain $\sigma_0 = \frac{K}{\pi}\left(\frac{\delta}{a} - \frac{a}{R}\right)$ and $\sigma_1 = \frac{K}{\pi}\left(\frac{2a}{R}\right)$. Therefore, the elastic energy follows from

$$U_{el} = \frac{1}{2}\int d^2\mathbf{x}\, u_z(\mathbf{x})\sigma_z(\mathbf{x}) = K\left[\delta^2 a - \frac{2}{3}\frac{\delta a^3}{R} + \frac{1}{5}\frac{a^5}{R^2}\right] = \frac{8}{\sqrt{3}}\,KR^3\,\Phi(h/2R), \qquad (5)$$

where in the last line, we have made used of the volume conservation constraint and $\delta = 2R - h$. Note that the elastic energy is a function of the height h only with a scaling function given $\Phi(x) \equiv \sqrt{x^{-1}-x^2}\left[(1-x)^2 - \frac{4}{9}(1-x)\left(x^{-1}-x^2\right) + \frac{4}{45}\left(x^{-1}-x^2\right)\right]$, which has the following asymtotics: $\Phi(x) \sim x^{-5/2}$, $x \ll 1$ and $\Phi(x) \sim (1-x)^{5/2}$, $x \sim 1$. We have made the following assumptions in deriving Eq. (5): First, we have employed linear elasticity theory as in the Hertz and JKR theory. Secondly, in calculating the displacement field in Eq. (4), we have made use the results from the half-space elastic medium. For small deformation, these assumptions are certainly justified, and the scaling of free energy Eq.(5) with h is in fact identical to the Hertz theory [13]. For large deformation, it can be argued that Eq. (5) should at least give the right scaling with h. To see this, consider an elastic ball which develops a contact radius of $a^2 \sim R^3/h$ for large deformation; the strain is then of the order of $\epsilon \sim a/R$. In a linear theory, the elastic energy must scale like $U_{el} \sim a^3\epsilon^2 \sim h^{-5/2}$, as obtained above. We note that in contrast to Hertz theory, Eq. (5) diverges as $h \to 0$. As we shall see below, even with this crude estimate of the elastic energy, our results compare quite well with the experimental data.

Results and Discussion. – The equilibrium contact angle θ follows from minimization of $U_{tot}(h) = U_s(h) + U_{el}(h)$ with respect to h. Figure 5 shows θ as a function of $2\sqrt{3}\,KR/(\pi\gamma_s)$ for different values of the reduced spreading parameter S/γ_s. First, we note that the contact angle is uniquely determined only if S, γ_s, R, and K are specified. In the limit $K \to 0$, we recover the contact angle as obtained from Young's law but it increases nonlinearly with K. This behavior is consistent with experimental observations. For $S > 0$, which corresponds to complete wetting for an ordinary liquid, the contact angle for the latex particles remains finite for finite K. Moreover, in the limit $S \gg KR$, the height of the latex particle follows an asymptotic scaling law of $h \sim R(KR/S)^{2/3}$.

Our model may provide a way of estimating the adhesion energy W. Indeed, we expect

that work is needed to deform the latex particles, and therefore, some of the gain in the surface energy must be converted into elastic energy. This implies that the work of adhesion W must be greater than that estimated by the Dupré formula, which only involves the surface tension. Note that our experiments are in an intermediate regime where both the surface tension and elastic energy are important and our model takes both into account. For an estimate, taking typical values from the latex experiments: $h/R \sim 0.3$, $R \sim 10^{-7}\,\mathrm{m}$, $K \sim 10^{6}\,\mathrm{Pa}$ and $\gamma_s \sim 50\,\mathrm{mJ/m^2}$, we find $W_D \sim 100\,\mathrm{mJ/m^2}$ from Dupré formula, and $W \sim 240\,\mathrm{mJ/m^2}$ from our model. Thus, their values are significantly different with W being twice as big as W_D. To test our model more quantitatively, we have compared our predictions to the experimental data for the latex particles as listed in Table II. The contact angle is obtained from the experimental values of the height, and it is used to deduce the spreading parameter S for a given K. The work of adhesion W follows from the relation $W = S + 2\gamma_s$. It should be noted that a direct experimental verification of our model would be to keep K, γ_s, and W fixed, while varying the particle radius R, so that the experimental measurement of the contact angle could be compared with only one of the curves shown in Fig. 5. Unfortunately, in the data obtained so far, the latex particles come in different sizes; this direct test will be further explored in the future. However, using the obtained values of W, we can estimate the contact radii using a formula from the JKR theory: $a_0/R = [9\pi W/(2KR)]^{1/3}$, and compare this to the experimental measured contact radius. The results are shown in Fig. 6, where W is estimated from the Dupré formula, and Fig. 7, where W is obtained from our theory. It is evident that using our model to predict W fits the experimental data quite well.

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